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Frit 625 Manufacturability Study

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EXECUTIVE SUMMARY

Based on the anticipated higher sodium concentration salt stream coming to the Defense Waste Processing Facility (DWPF) from the Salt Waste Processing Facility (SWPF), there may be a future need to reduce the alkali concentration in the frit depending on the composition of the sludge in Tank 40. SWPF is projected to start operating in late 2019. Thus, a lower alkali frit is beneficial for Sludge Batch (SB9) processing. Lower alkali frits may also be needed for Sludge Batch 10 (SB10) and later batches to ensure that the composition of the material in the Slurry Mix Evaporator (SME) is acceptable relative to the Product Composition Control System (PCCS) models.

Prior to the processing of SB9 with Frit 803 at DWPF, assessments and experimental glass work were completed to support SB9 coupled processing with streams from the Actinide Removal Process and Modular Caustic Side Solvent Extraction Unit. Since that time, additional Tank 40 analyses were completed, which served as the basis for an updated projection of the SB9 blend composition in Tank 40. Using this projection from Savannah River Remediation, the Savannah River National Laboratory (SRNL) conducted a paper study to select a second frit to optimize the upcoming SB9 coupled operation with the Salt Waste Processing Facility. Frit 625 was recommended based on the results of assessments using the current DWPF Product Composition Control System models and their associated Measurement Acceptance Region constraints. Compared to Frit 803, Frit 625 includes Al_2O_3 and has a slightly lower total alkali concentration (sum of Li_2O and Na_2O).

The objective of this experimental work was to confirm that the high temperature viscosity of Frit 625 is acceptable for manufacturing at DWPF's frit supplier (currently Bekeson Glass LLC). Additional frits were included to provide guidance for frit development efforts for SB10 and beyond. Frit 625 was batched from reagent-grade chemicals and melted at 1300°C at SRNL. Viscosity measurements were collected in 50°C increments throughout the temperature interval of 1250-1500°C. The viscosity of Frit 625 was 191 Poise at 1250°C and 32 Poise at 1500°C.

Based on the high temperature viscosity profile of Frit 625, the current DWPF frit supplier (Bekeson Glass LLC) has confirmed that this composition ($1Al_2O_3$-$8B_2O_3$-$7Li_2O$-$6Na_2O$-$78SiO_2$, in weight percent) is acceptable for manufacturing. Additional frits besides Frit 625 were included in this study to gain supplementary viscosity information as a function of composition for future frit development efforts. The impact of adding an additional 3 weight percent Al_2O_3 to Frit 625 (Frit C testing) is minimal. Thus, the composition of Frit 625 would still have an acceptable viscosity if the Al_2O_3 concentration reaches the upper limit of the frit specification acceptance tolerance. Higher Al_2O_3 concentration frits could also be of interest for future sludge batch processing.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
DWPF	Defense Waste Processing Facility
MCU	Modular Caustic Side Solvent Extraction Unit
MST	monosodium titanate
NIST	National Institute of Standards and Technology
PCCS	Product Composition Control System
SB9	Sludge Batch 9
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility
wt.%	weight percent

1.0 Introduction

Based on the anticipated higher sodium concentration salt stream coming to the Defense Waste Processing Facility (DWPF) from the Salt Waste Processing Facility (SWPF), there may be a future need to reduce the alkali concentration in the frit depending on the composition of the sludge in Tank 40. SWPF is projected to start operating in late 2019. Thus, a lower alkali frit is beneficial for Sludge Batch (SB9) processing. Lower alkali frits may also be needed for Sludge Batch 10 (SB10) and later batches to ensure that the composition of the material in the Slurry Mix Evaporator (SME) is acceptable relative to the Product Composition Control System (PCCS) models.[1]

Prior to the processing of Sludge Batch 9 (SB9) with Frit 803 at the Defense Waste Processing Facility (DWPF), assessments and experimental glass work were completed to support the qualification of SB9 coupled processing with streams from the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU).[2-6] This previous work did not address coupled processing with streams from the SWPF because PCCS models limited the TiO_2 concentration in glass to 2 weight percent (wt.%).[7] These high activity streams from SWPF include monosodium titanate (MST) and sludge solids from the Sludge Solids Receipt Tank as well as Cs-containing strip effluent. The incorporation of these SWPF streams is expected to reach TiO_2 concentrations in glass greater than 2 wt.% based on an MST strike of 0.4 g MST/L of salt solution. Therefore, revisions to the models contained in PCCS were completed to allow the evaluation of glasses containing greater than 2 wt.% TiO_2, but less than 6 wt.%.[1]

Since the initial SB9 qualification for ARP-MCU coupled operation, additional Tank 40 analyses were completed, which served as the basis for an updated projection[8] of the SB9 blend composition in Tank 40. Using this projection from Savannah River Remediation, the Savannah River National Laboratory (SRNL) conducted a paper study to select a frit to optimize SB9 coupled operation with SWPF. Frit 625 was recommended[9] based on the results of assessments using the current DWPF PCCS models and their associated Measurement Acceptance Region constraints.[1] Compared to Frit 803, Frit 625 includes Al_2O_3 and has a slightly lower total alkali concentration (sum of Li_2O and Na_2O). While SB10 is still in the preliminary planning stages, Frit 625 will also be evaluated to determine whether it is a viable option for SB10 coupled operation with SWPF.

The objective of this experimental work was to confirm that the high temperature viscosity of Frit 625 is acceptable for manufacturing at DWPF's frit supplier (currently Bekeson Glass LLC). Additional frits were included to provide guidance for frit development efforts for SB10 and beyond.

2.0 Quality Assurance

This work was requested via a Technical Task Request[10,11] and directed by a Task Technical and Quality Assurance Plan.[12] The functional classification of this task is Production Support. This task is not waste form affecting and does not need to follow the quality assurance requirements of RW-0333P.[13] Microsoft Excel was used to support this work. Data are recorded in the PerkinElmer E-Notebook under experiment C7592-00311-28. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[14] This document, including all Microsoft Excel calculations, was reviewed by a Design Check. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[15]

3.0 Experimental Procedure

3.1 Target Frit Compositions

Target compositions of the frits included in this study are shown in Table 3-1 in weight percent (wt.%). Additional frits besides Frit 625 were included to gain supplementary viscosity information as a function of composition for future frit development efforts. A brief description of each composition follows.

1. Frit 625 was recommended for SB9 coupled operation with SWPF (optimized to Cases #1-5, with Case #3 set to 600 mg/L of entrained insoluble sludge solids).[9]
2. Frit A was identified as another viable composition for SB9 coupled operation with SWPF (optimized to Cases #1-5, with Case #3 set to 1200 mg/L of entrained insoluble sludge solids).[9]
3. Frit C is the same composition as Frit 625, but with a higher Al_2O_3 concentration.
4. Frit C2 is the same composition as Frit C, but with a higher B_2O_3 concentration.
5. Frit D has a lower total alkali concentration (Li_2O + Na_2O) than all other frits included in this study.
6. Frit 803 is the frit currently used for SB9 coupled operation with ARP-MCU and is included as a control.

Note that the SiO_2 concentrations of the frits were adjusted to accommodate the changes in Al_2O_3, B_2O_3, and alkali concentrations.

Table 3-1. Target Frit Compositions (wt.%)

Frit ID	Al_2O_3	B_2O_3	Li_2O	Na_2O	SiO_2
Frit 625	1	8	7	6	78
Frit A	2	9	8	6	75
Frit C	4	8	7	6	75
Frit C2	4	12	7	6	71
Frit D	----	8	5	5	82
Frit 803	----	8	6	8	78

3.2 Glass Fabrication

Each batch was prepared from the proper proportions of reagent-grade chemicals.[16] The raw materials were blended in a shaker-mixer for 10 minutes with zirconia ball media and then placed into a uniquely identified platinum alloy crucible. Each crucible was covered with a loose-fitting lid and placed into a pre-heated high-temperature furnace at the desired melt temperature for one hour.[17] All frits were melted at 1300°C, except for Frit D, which was melted at 1450°C due to residual unmelted material at 1300°C. A sample of Frit 803 manufactured at Bekeson Glass LLC (Lot B080)[18] was also melted at 1300°C. At the end of the isothermal hold, the crucibles were removed, and the molten glass was poured onto a clean, stainless steel plate. The melt was allowed to cool to ambient temperature.

3.3 Viscosity

The viscosity versus temperature relationship was measured for each frit in ~50 degree increments using a rotating spindle viscometer in the range of 1250-1500°C.[19] A silicone viscosity standard fluid, traceable to the National Institute of Standards and Technology (NIST), was used to verify the operation of the viscometer at room temperature prior to use. The NIST 711 glass viscosity standard[20] was measured before and after the frit samples to determine the pre- and post-measurement spindle constants (K). Three torque measurements were collected at each temperature. A hysteresis approach was used during sample data collection to determine whether volatility or crystallization was an issue throughout the course of the measurement period. Thus, measurements were collected in the following order: 1450°C, 1500°C, 1450°C, 1400°C, 1350°C, 1300°C, 1250°C, and 1450°C. Viscosity (η) was calculated using both the pre- and post-measurement spindle constants (K) with the equation given by:[21]

η (Poise) = K(T) × (percent (%) torque) / (rotation speed)

where K(T) is a linear equation for the spindle constant (K) as a function of temperature (T), which was determined using the equation above and the published viscosity values for the NIST traceable silicone viscosity standard fluid and NIST 711 glass viscosity standard.

4.0 Results and Discussion

Photographs of the as-fabricated glasses are shown in Figure 4-1. Frit D had an opalescent appearance, which is an indicator of phase separation. The remainder of the glasses were transparent with the presence of small bubbles within the glass matrix that are commonly observed in laboratory-scale melts.

The average measured viscosity (η) data were fit with the Arrhenius equation given by:

$$\ln \eta = A + B \times 10^3/T$$

where *A* and *B* are constants and *T* is temperature in Kelvin.

Frit 625

Frit A

Frit C

Frit C2

Frit D

Frit 803

Figure 4-1. Photographs of the as-fabricated glasses.

Details of the linear regression for each frit are shown in Appendix Figure A-1 through Figure A-6. The R^2 values are 0.98-1, which demonstrates that there is little difference between the measured and fitted values. Crystallization or volatility do not appear to be an issue since there are negligible differences in the multiple data points collected at 1450°C. The presence of phase separation in Frit D did not impact the Arrhenius behavior of viscosity in the temperature region evaluated.

Table 4-1 shows the resulting fitted viscosity values for each of the six frits as a function of temperature. The data for Frit 803 are consistent with the values shown for a sample of Frit 803 that was measured in 2012.[22] Reduction of alkali (Li_2O and Na_2O) in Frit D results in the highest increase in viscosity of the frits evaluated. The impact of adding an additional 3 wt.% Al_2O_3 to Frit 625 (Frit C) is minimal.

Table 4-1. Viscosity (Poise) as a Function of Temperature

Frit ID	Temperature					
	1250°C	**1300°C**	**1350°C**	**1400°C**	**1450°C**	**1500°C**
Frit 625	191	128	88	62	44	32
Frit A	120	81	56	40	29	21
Frit C	205	134	90	62	44	31
Frit C2	127	86	59	42	30	22
Frit D	498	323	215	147	103	73
Frit 803	139	95	66	47	34	25
Frit 803 (2012)[22]	141	94	64	45	32	23

5.0 Conclusions

Based on the high temperature viscosity profile of Frit 625, the current DWPF frit supplier (Bekeson Glass LLC) has confirmed that this composition is acceptable for manufacturing.[23] The impact of adding an additional 3 wt.% Al_2O_3 to Frit 625 is minimal. Thus, the composition of Frit 625 would still have an acceptable viscosity if the Al_2O_3 concentration reaches the upper limit of the frit specification acceptance tolerance. These data will support frit development efforts for SB10 and later sludge batches.

6.0 References

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Appendix A. Predicted ln (viscosity in Poise) versus 1000/T (K^{-1}) for Each Frit Using the Arrhenius Equation

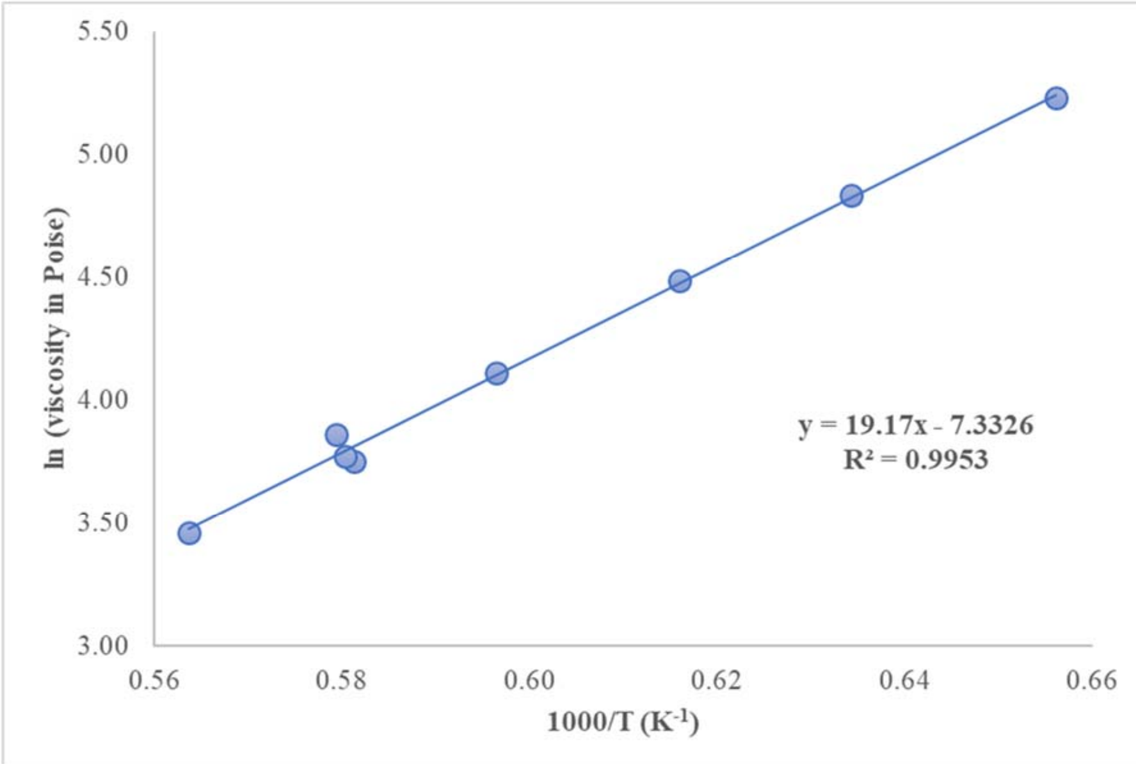

Figure A-1. Linear fit for Frit 625.

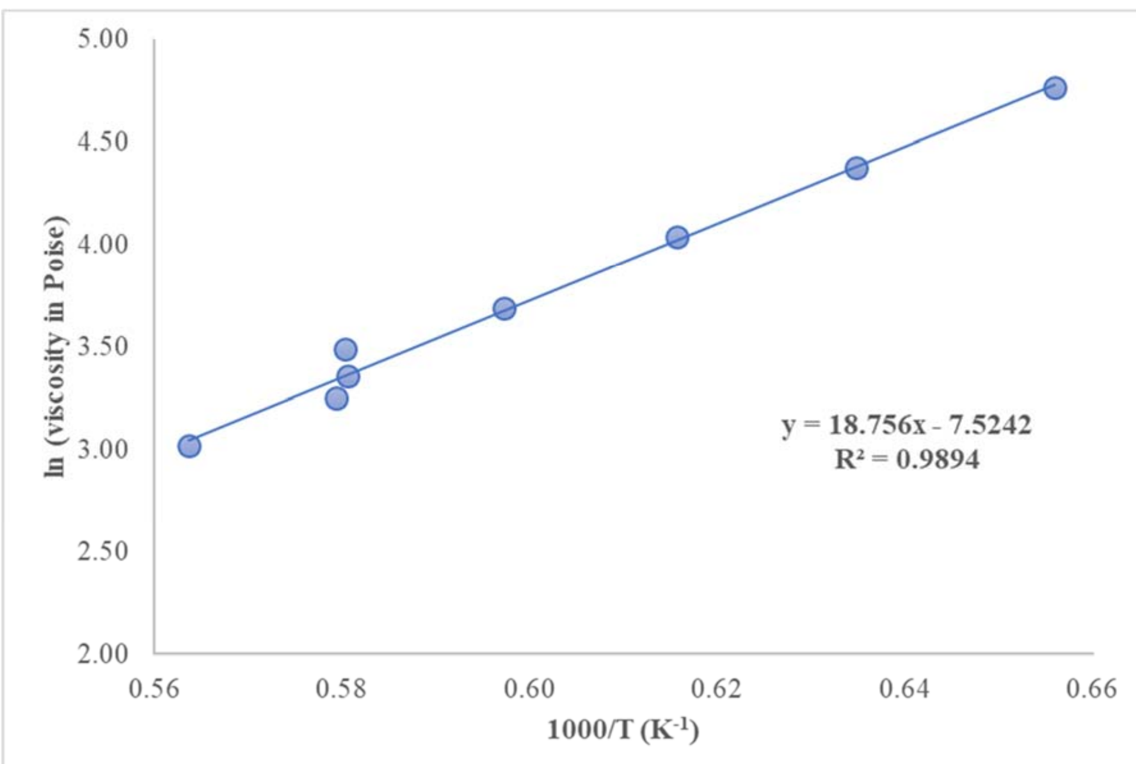

Figure A-2. Linear fit for Frit A.

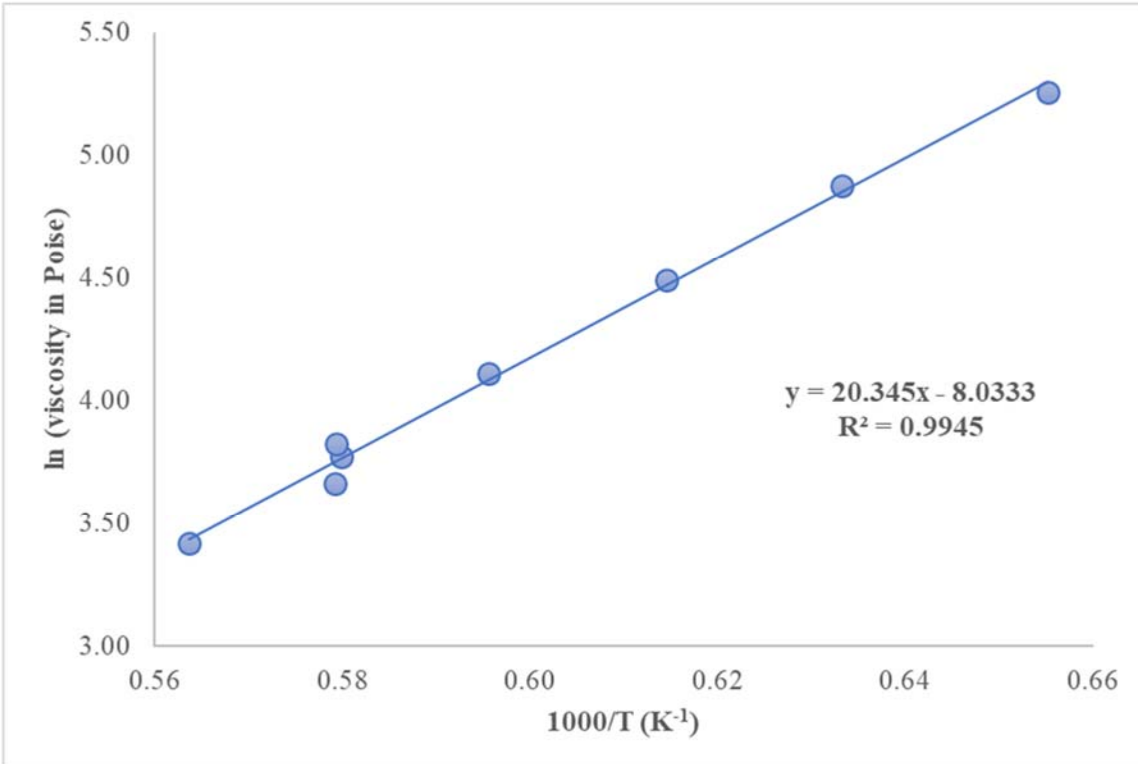

Figure A-3. Linear fit for Frit C.

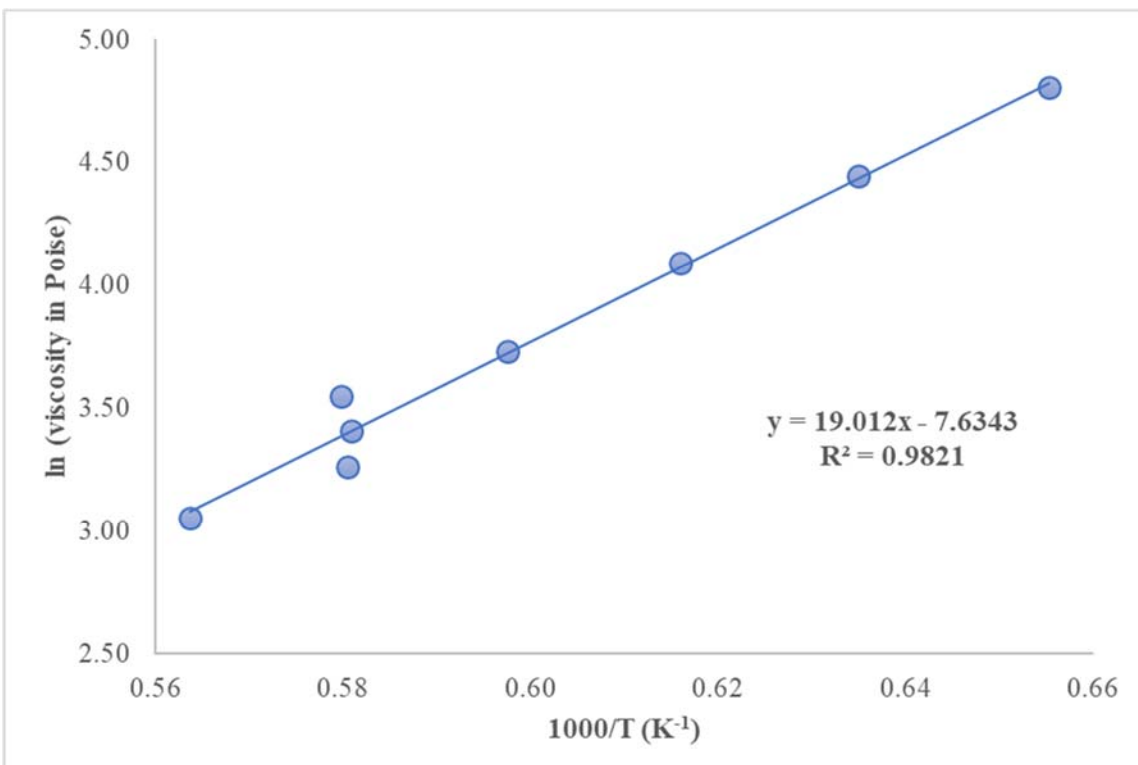

Figure A-4. Linear fit for Frit C2.

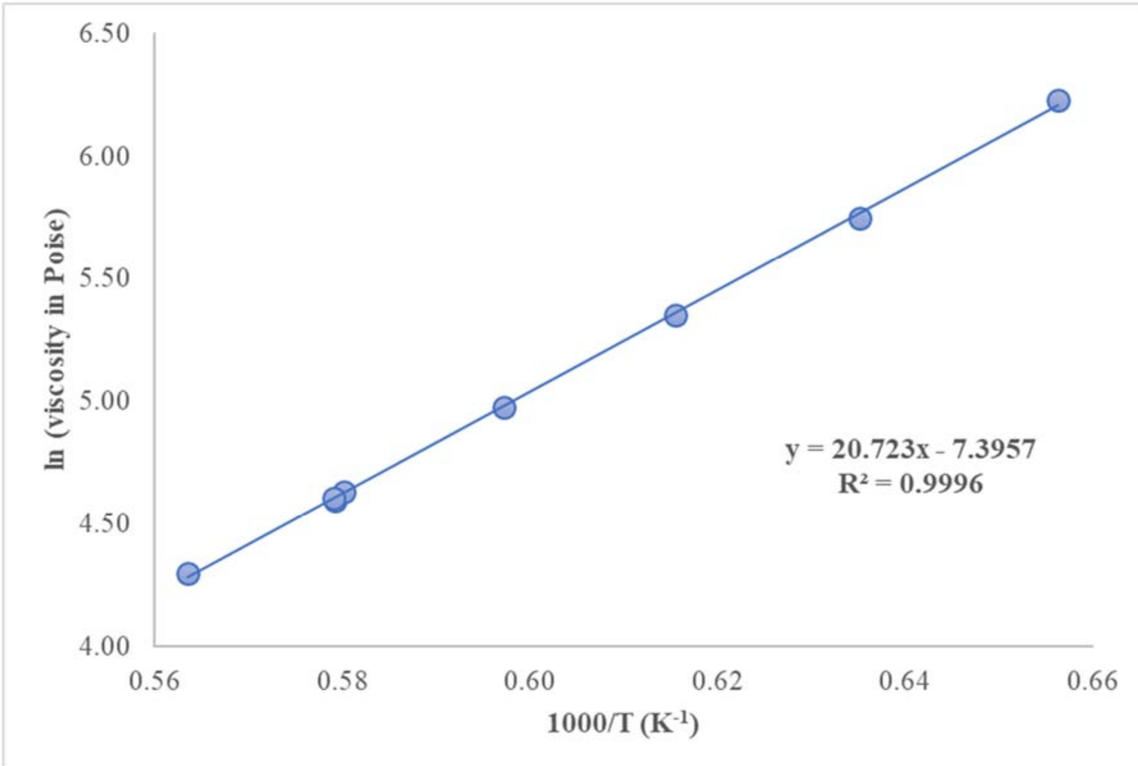

Figure A-5. Linear fit for Frit D.

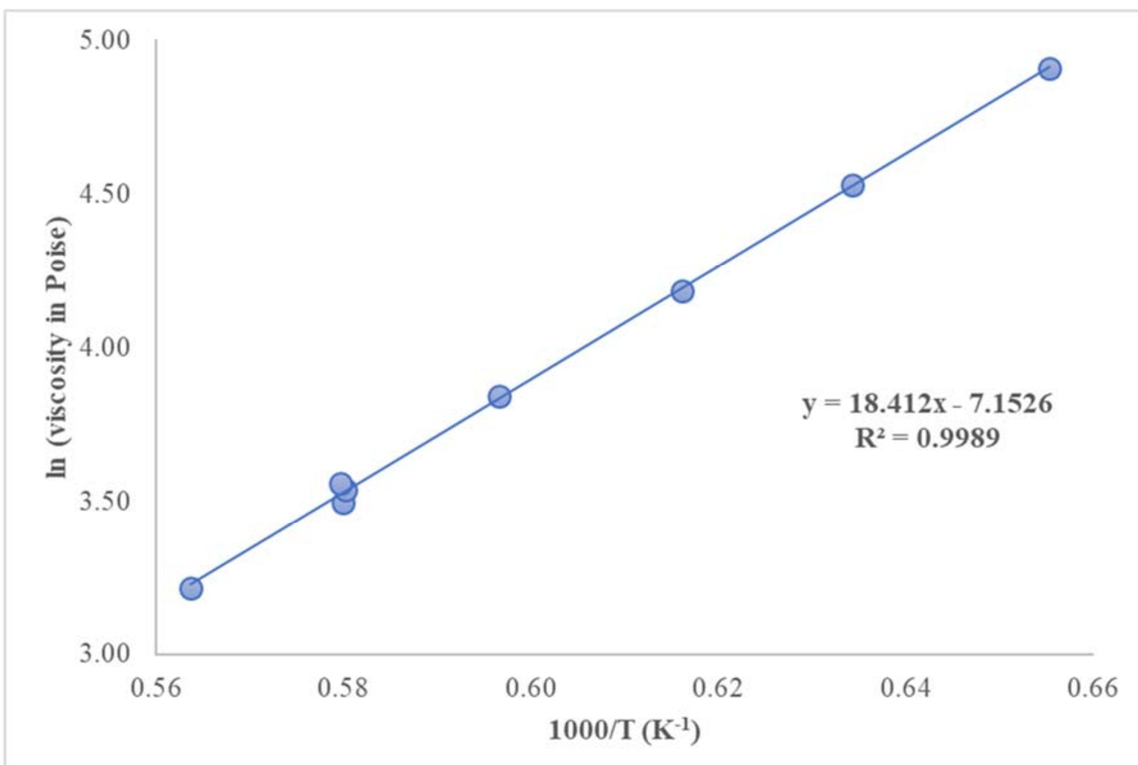

Figure A-6. Linear fit for Frit 803 (measured in 2019).

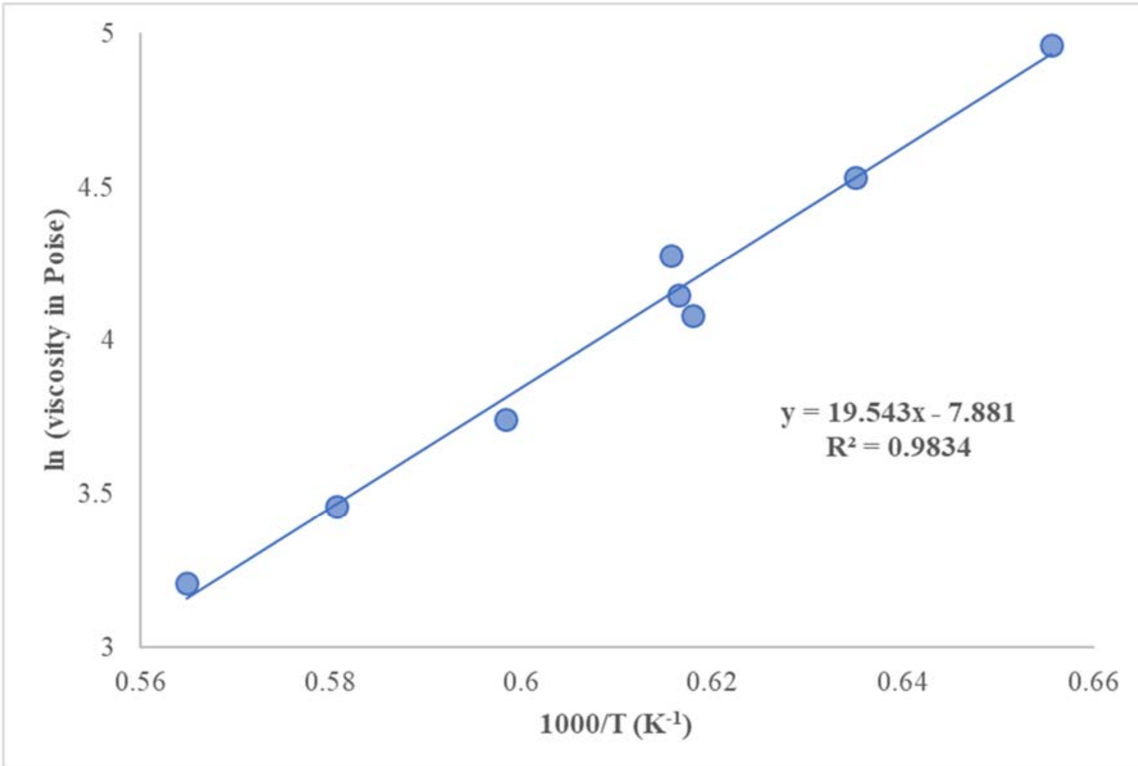

Figure A-7. Linear fit for Frit 803 (measured in 2012).